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Interaction of water molecules with SiC(001) surfaces

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ABSTRACT.

We have investigated the interaction of water molecules with the polar Si- and C- terminated surfaces of cubic Silicon Carbide by means of *ab initio* molecular dynamics simulations at finite temperature. Different water coverages were considered, from $\frac{1}{4}$ to a complete monolayer. Irrespective of coverage, we find that water dissociates on the silicon terminated surfaces, leading to important changes in both its structural and electronic properties. On the contrary, the carbon terminated surface remains inert when exposed to water. We propose experiments to reveal the ionic and electronic structure of wet Si-

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terminated surfaces predicted by our calculations, which at full coverage are notably different from those of hydrated Si(001) substrates. Finally, we discuss the implications of our results for SiC surface functionalization.

KEYWORDS: chemisorption, water, silicon carbide, ab-initio molecular dynamics.

I. Introduction

The interaction of water with semiconductor surfaces plays a key role in many fields, ranging from well established processes used in the semiconductor industry to functionalization of substrates for the detection of chemical and biological agents and the realization of MEMS¹ (Micro-Electro-Mechanical Systems) and possibly NEMS (Nano-Electro-Mechanical Systems).

From a theoretical stand-point, the study of water/semiconductor interfaces and interactions is in its infancy, because of inherent difficulties in accurately describing such complex systems at the microscopic level, and for the large computational effort usually involved. While water adsorption on metal² and elemental semiconductors surfaces, such as Si(001)³ and C(001)⁴ has been studied in some detail, only few investigations have addressed the problem of water interaction with polar surfaces⁵⁻⁸.

It has recently been established that water is preferentially adsorbed via a dissociative chemisorption process on both silicon³ and diamond⁴ (001) surfaces. By means of several *ab initio* methods, and often comparing a number of theoretical approaches, from Hartree-Fock, to Density Functional Theory (DFT), it has been shown that for the Si(001) surface the molecular precursor state is an intermediate state towards the dissociated chemisorption of an OH radical and an H fragment; this fragment bonds preferentially to the same surface dimer, with the hydroxyl group pointing away from the surface dimer. On the contrary, on diamond (001) surfaces⁴ dissociation is unlikely to occur because of a high activation energy barrier, although it is energetically favored. Water interaction with ionic surfaces such as NaCl or KCl⁷ leads to molecular adsorption, with oxygen preferentially close to the cation, and geometric details that critically depend on water coverage. On MgO instead, while physisorption has

been the only observed interaction at the ideal surface, dissociation may occur when defects (such as steps) are present⁸.

Given the differences observed in water interactions with semiconductor and ionic surfaces, it is interesting to investigate the role played by the substrate ionicity. Silicon Carbide can be considered as the template for water interaction with a wide band-gap semiconducting surface: although a compound semiconductor of group IV, SiC bonds are highly ($\sim 15\%$) ionic⁹. In addition, the cubic polytype (β -SiC) is made of alternating C and Si layers, giving rise to two (001) surfaces with rather different electronic and structural properties¹⁰. SiC is receiving widespread attention as a promising biocompatible material¹¹. However, at present only one theoretical attempt to study SiC surfaces functionalization is available¹², and even the microscopic characterization of H₂O/SiC interfaces is still in its initial stages¹³, since it is extremely challenging, both from an experimental and a theoretical standpoint. We have recently presented results for the interaction of gas phase water with SiC(001) surfaces, outlining which experiments could detect specific changes in both structural and electronics properties of the SiC(001) surfaces¹⁴. Here, we provide a thorough description of our investigation, and we describe in detail both the simulation of adsorption mechanisms and reaction paths, as well as the modifications of the surface geometry induced by the presence of a full water monolayer. In addition we present a qualitative analysis of the stretching mode frequencies of $-H$ and $-OH$ groups on Si-SiC(001) surfaces, and we discuss possible surface oxidation processes that take place in wet ambient. Our study is performed by parameter-free molecular dynamics at finite temperature, and it goes beyond the determination of static structures, thus allowing for the description of realistic dissociation paths. We considered both Si- and C-terminated surfaces in their stable $p(2\times 1)$ and $c(2\times 2)$ surface reconstructions¹⁰, and we investigated different molecular coverages. Irrespective of the coverage, we found that water molecules dissociate on the Si-terminated [Si-SiC(001)] surface and that at high coverage full hydroxylation occurs via a proton exchange mechanism similar to that found on alumina⁶. On the other hand, water dissociation is found to be an activated process on the C-terminated [C-SiC(001)] surface, and it is very unlikely to occur even at high temperature. When further dissociation

of the hydroxyl groups is simulated, we obtain a preferential oxidation of the Si-terminated surface in wet ambient. Finally, we performed similar calculations for the clean Si(001) surface at high water coverages: our results reveal remarkable differences between the pure covalent silicon and the polar compound. The rest of the paper is organized as follow: in Section II the calculation method is briefly presented; in Section III and IV we present results for the interaction of water molecules with the Si- and C- terminated SiC(001) surfaces respectively; Section V describes further oxidation processes that may occur in wet ambient at the SiC(001) surfaces; finally, conclusions are outlined in Section VI.

II. Method

Our calculations were performed using Density Functional Theory with the Generalized Gradient corrected functional (GGA) recently proposed by Perdew et al.¹⁵ (hereafter referred at as PBE approximation).

In our simulations, the SiC(001) surfaces were represented by a symmetric slab, periodically repeated along the (001) direction. We used supercells with 11 layers, 8 atoms/layer and a ~ 12.5 Å vacuum region, between the clean surfaces. Calculations at high water coverages were performed on an 11 layers, 16 atoms/layer slab, with the same vacuum region, to allow for a more disordered distribution of molecules. The large in-plane size was chosen with two purposes: (i) at low coverages, it allows for the study of isolated water molecules, avoiding the interaction of a molecule (or dissociated radicals) with its periodic replicas; (ii) it provides a good sampling of the clean surface unit cell, even when including only the Γ point of the supercell in Brillouin Zone integration, as in the present case (this corresponds to 3 (6) inequivalent k-points in the primitive cell, for the supercell with 8 (16) atoms/layer).

The geometry of all configurations was optimized using *ab initio* molecular dynamics¹⁶ at the theoretical equilibrium lattice parameter. We used nonlocal pseudopotentials¹⁷ (*s* and *p*, and *s* nonlocality for Si and O, C, H respectively) derived within the PBE approximation. The electronic wavefunctions and charge densities were expanded in plane waves, with energy cutoffs (E_{cut}) up to 80 and 320 Ry, respectively. All atoms were allowed to move, and geometries were considered at

convergence when forces were less than 10^{-4} a.u./atom and the energy varied less than $3 \cdot 10^{-5}$ eV/atom.

We verified that treating spin explicitly does not affect the results presented here.

Accuracy tests were performed on both the clean silicon and carbon terminated SiC(001) surfaces and on the H₂O molecule. As for the clean surfaces, we compared our results with those obtained with previous LDA¹⁸ and PBE¹⁹ calculations, obtaining an overall agreement with the previously published results. In particular the Si-SiC(001) surface presents long (~ 2.64 Å) slightly buckled (~ 0.01 Å) Si dimers, while the clean C-term surface shows *sp* bonded C unbuckled dimers, 1.24 Å long. As described elsewhere^{10,18}, within the LDA, the Si-SiC(001) has a small band gap between antibonding surface states with $\pi^*_{x,y}$ and $\pi^* + \sigma$ character localized on dimers, with partial bonding charge along the dimer rows. On the contrary, the unusual *sp* bridge C-SiC(001) reconstruction shows different electronic features, with a prominent π_z character on C dimers, and π_x on the Si underlying dimers, with a wide gap opening between π_z and π_z^* states. Tests on the water molecule included the geometry of a single molecule, the determination of minimal cell dimensions to avoid interaction between replicas, the water dimer and liquid in normal conditions: the results agree well with previously published work²⁰.

III. Adsorption of water at the Si-SiC(001) Surface

A. Low coverage. We have first investigated the reaction of water molecules with the Si-SiC(001) surface at $\sim 1/4$ ML coverage (i.e. one water molecule for each surface dimer). We considered different orientations of the plane defined by the water molecule (parallel or perpendicular to the surface), and we let the molecule impinging on the surface by exposing either the oxygen or hydrogen atoms, at different adsorption sites on the surface unit cell: on dimers, between dimers of the same row and between adjacent dimers. The molecule experiences an attractive interaction while impinging on the surface: our results indicate that even at the largest distance considered here (H₂O at 5.8 Å) the interaction surface/molecule is not negligible: the Si-dimers become shorter in the relaxed configuration (~ 2.58 Å, i.e. 12 % less than in the clean case) and buckled. Furthermore, for the water molecule it is favorable to approach the surface by exposing the oxygen atom rather than the H atoms, as it appears evident by simple inspection of the molecular dynamics simulation.

As the distance from the Si surface atoms decreases, at nearly zero temperature, the molecule spontaneously dissociates, following different possible paths. The analysis of the intermediate configurations found along the reaction path revealed that, regardless of the surface adsorption site, a common water/surface interaction mechanism takes place, which involves attractive electrostatic forces between the water molecules and the Si-SiC(001) surface. When the molecule approaches the surface, major rearrangements are observed in the surface geometry: the weak Si dimers are shortened up to 2.44 Å, and buckled (maximum buckling $\sim 4^\circ$ - $\Delta z \sim 0.2\text{\AA}$). In all cases we observed that the oxygen atom of the water molecule, which is electron rich, interacts with the down atom of the buckled surface Si dimer which becomes electron poor, as it is shown below. The minimum Si-O distance observed before dissociation was $\sim 1.9\text{\AA}$; at this short distance a dative bond is likely to be established between one oxygen lone pair and the empty state localized on the surface silicon atom. In Fig. 1 a snapshot of the simulation run is shown: in this geometry one of the water O-H bond is oriented nearly parallel to the underlying Si-Si surface bond, with Si \cdots O and Si \cdots H distances of 2.67 and 2.62 Å, respectively. Upon adsorption, the Si dimer buckles out (3.8° - $\Delta z = 0.16\text{\AA}$) with the up atom oriented towards the H atom and the down atom facing the oxygen one. The induced buckling imparts a polarity to the dimer due to an electronic transfer occurred from the down to the up Si atom, which is responsible for the Si-Si bond shortening and the attractive polar interaction with the adsorbed water molecule. Such electronic transfer is revealed by the presence of occupied electronic states close to the highest occupied molecular orbital (HOMO, see for example Fig. 1) where a heap of electronic charge on the up Si atom of the dimer is found.

Irrespective of the impinging position at the surface, the water molecule diffuses on the surface until it finds a favorable dissociation site²¹: the molecule then spontaneously breaks in two fragments (-H and -OH) bonded to two adjacent Si atoms. At this low coverage, we observed three possible dissociation products which differ for the relative position of the -H and -OH groups, as reported in Fig. 2. However, the local geometry of the dissociation product is similar: in the final configuration a Si-O bond 1.66 Å long, and a Si-H 1.49 Å long are formed. Moreover, the Si dimers involved are strengthened with

respect to the free surface, being 2.46 Å long, with a maximum buckling of 2.3° ($\Delta z = 0.1$ Å). The energy gain upon dissociation is also similar in the three configurations, being -3.2, -3.3 and -3.5 eV/molec (-74.3, -77.2 and -80.2 Kcal/mol) for the a) b) and c) products of Fig. 2 respectively.

A.1 Comparison with H₂O/Si(001)

The Si-SiC surface presents similarities with the Si(001) surface, where the water molecule was found to dissociate after forming a transient molecular physisorbed state³. Nevertheless the details of the dissociation mechanism and the final product differ. Indeed the clean silicon surface presents buckled dimers which elongate when interacting with the water molecule, reducing their tilt to zero as the molecule dissociates³. Furthermore, in the silicon case, only the product with the -H and -OH fragments bound to the same surface dimer was found to be energetically favorable; on the Si-SiC surface this is the most unfavorable configuration (case a) of Fig. 2). This may be due to the higher distance among Si-Si surface dimers which makes the reaction path to the b) and c) products of Fig. 2 impossible in silicon. At this low coverage, on Si-SiC(001) we have observed that major distortions can be induced by the presence of the -OH group to the nearby surface reconstruction. In particular for the structure a) of Fig. 2 we observed that the hydrogen atom of the -OH fragment directly points to the Si atom of the adjacent Si-Si dimer, which deeply changes, being 2.43 Å long and highly buckled (11° - $\Delta z = 0.46$ Å), with the up atom facing the -OH fragment. This rearrangement seems to reveal that a hydrogen bond like (-OH ... Si) interaction has occurred, characterized by an O ... Si distance of 3.6 Å (H ... Si 2.94 Å). Indeed the electronic structure analysis reveals that the up Si atom of this buckled dimer is electron rich, due to the Si-Si charge transfer induced by the buckling (see Fig. 3). This atom can thus act as a hydrogen acceptor and establish a hydrogen bond. The peculiar bond distances in SiC are responsible of the energy ordering of the three metastable structures a-c: configuration c) is the most stable: the O ... Si distance is optimised for the formation of H-bond, the repulsive interaction between -OH and -H is weakened, if compared to b); moreover, two Si-dimers are strengthened in b) and c) giving rise to further energy gain with respect to a).

A.2 Implications for structural properties of “dirty” Si-SiC surface

Several reconstructions have been found to occur at the Si-SiC(001) surface, depending on the fractional Si coverage, and preparation conditions²². Furthermore, controversies are still open on the most stable geometries, both from the experimental and theoretical points of view¹⁰. On the stoichiometric Si-SiC(001) surface, dimerization of surface Si atoms induces a p(2x1) periodicity: a structural analysis of the p(2x1) pattern has led to a buckled-dimer model similar to that of Si(001)²³. However this model has not been confirmed by *ab initio* calculations^{18,19,24}, reporting instead unbuckled dimers much longer than those of Si(001); moreover recent ARUPS data²⁵ are consistent with a weak bonding of unbuckled Si dimers. Core Level photoemission spectroscopy²⁶ suggests that the stable reconstruction for the clean stoichiometric Si-SiC(001) surface should be a c(4x2) geometry, p(2x1) occurring in presence of defects, consistently with recent STM data²⁷. Several models for the c(4x2)-SiC(001) reconstruction have been recently proposed based on different experimental data; STM and photoemission experiments are consistent with a geometry of alternating symmetric dimers (AUDD) with different heights^{18,19,27}. ARUPS measurements on different samples²⁸ are however in accord with a model of bridging, buckled dimers²⁹. The surface reconstruction that occurs upon water adsorption, which involves a transition from long-flat to short-buckled Si dimers, can be in part responsible of this long-standing controversy about structural data of Si-SiC(001), since water (aqueous vapor) is a normal contaminant even in UHV conditions.

B. ½ ML coverage. We have further studied higher water coverages: we considered two water molecules per supercell, analysing the possible interaction between the dissociated fragments. In particular we studied configurations with neighboring or distant –OH fragments and we found that the structures with two –OH attached on adjacent Si atoms are the most stable (see Fig. 4). This is due to the formation of an H-bond between the –OH groups; this bond lowers the energy of the system by about 0.29 eV/OH (6.7 Kcal/mol) for interacting fragments bonded to adjacent dimers of different rows (right panel of Fig. 4), and by 0.23 eV/OH (5.4 Kcal/mol) for the H-bond formed along the dimer row (OH groups bonded to subsequent dimers along the same row, left panel of Fig. 4). This small but significant difference can be ascribed to geometrical factors; in fact in the first configuration a more

favourable interaction between –OH pairs is realized, with a O ... O distance of 2.71 Å (O ... H 1.73 Å), which is shorter than in the other configuration (O ... O 3.04 Å and O ... H 2.22 Å). This result indicates that for high water coverages, a process of “islanding” can take place, since the structures with neighboring –OH become more and more favored. In the case of the Si(001) surface, due to the larger lattice parameter, the H-bond between the –OH groups is weaker³ (-0.05 eV/molec , (O ... O) = 3.8 Å). Therefore ordered –OH patterns are more likely to be realised on Si-SiC(001) surfaces than in Si(001).

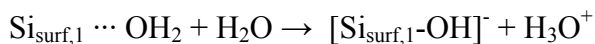
At this coverage, we also considered the reactivity of the surface to a hydrogen-bonded H₂O dimer, to understand if molecular dissociation could be inhibited in a "water like" environment, where hydrogen bonds among molecules are present. We observed the same reaction path towards dissociation found for a single molecule, and the same dissociation energy gain. This result indicates that the description of the water/surface interaction obtained for the vapour phase should still be valid when the contact with a liquid phase is considered. Our simulations indicate that, at least in the low coverage regime, the unimolecular dissociation dynamics is not strongly perturbed by the presence of additional adsorbed molecules.

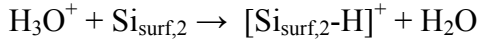
C. 1ML coverage. Inspired by the results on ordered islanding described above, we first simulated the deposition of 1ML of water molecules in an ordered and periodic structure on the Si-terminated surface. The molecules were adsorbed between dimer rows (trenches) in correspondence of the surface dimers at a starting Si ... O distance of 2.5 Å. As the simulation proceeds, all the molecules dissociate spontaneously in a collective way giving rise to a fully covered Si-SiC hydroxylized surface in a geometry very close to the one obtained at the lowest coverage: indeed in this case (see Fig. 5) we obtained Si-OH distances of 1.68 Å and Si-H of 1.49 Å, while the Si-Si dimers are shortened to 2.37 Å (buckling 0.01 Å). The dissociation energy per molecule is also similar to that at ¼ ML, namely –3.2 eV/molec (-73,6 Kcal/mol). It is interesting to note that, even at this high coverage, all the -OH groups attached to adjacent dimers become aligned along the dimer row and form one line of H-bond interacting fragments (O ... O 3.10 Å and H ... O 2.29 Å). Furthermore, due to the saturation of all the dangling bonds of the surface atoms upon water adsorption, at full coverage the optical gap of the

surface increases giving rise to a wide band gap substrate (the gap computed with the approximations used in our calculation is 1.6 eV³⁰). This increase may be observed in photoemission experiments. At variance with the clean Si-SiC surface, the highest occupied electronic states are surface π states strongly localized on Si dimers, which are shortened in this case. These states are hybridised with the oxygen p-orbital, giving rise to charge spilling around the –OH group (and in part at the Si-H complex, see Fig. 5) and are responsible for the STM image features that we discussed elsewhere¹⁴; in particular an STM tip would detect a bright spot localized between dimer rows, originating from the large contribution around the dissociated fragments.

We have then considered several 1ML configurations differing for the relative position of the –OH and the –H fragment at the Si surface. As expected, also at this coverage, we found that the configuration maximizing the number of H-bonds among the –OH fragments are the lowest in energy. In particular in both structures a) and b) of Fig. 6 four H-bonds per cell are present, and they are almost degenerate in energy, whereas the configurations c) and d), where smaller number of H-bonds (or weaker bonds) are present, are 0.25 eV/cell and 0.36 eV/cell higher in energy than configuration a). Similar calculations performed on the Si(001) surface yield remarkably different results: no spontaneous dissociation occurs on silicon when the surface is exposed to 1ML water coverage, and, as previously stated, –OH fragment islanding is energetically less favored.

To make contact with more realistic experimental conditions, i.e. the deposition of 1ML of water in the vapour phase, we have also simulated the adsorption of a randomly oriented layer of water molecules on the Si-SiC surface, i.e. 4 molecules per each c(4x4) surface: this corresponds to a monolayer at the density of liquid water at room T ($\sim 1 \text{ g/cm}^3$). The simulation started with molecules at an average distance of 2.5 Å from the substrate, and an O ... H distance larger than 2.1 Å. During the simulation time ($\sim 1.5 \text{ ps}$), we observed that at such high coverage the dissociation process may occur through a mechanism of proton exchange among the water molecules close to the surface, which can be summarized as follows:





where $\text{Si} \cdots \text{OH}_2$ indicates a physisorbed molecular state. The surface acts as an electron and a hole acceptor in the first and second step of the reaction, respectively, and the system remains globally neutral. In some cases we observed that the two initial steps take place in a synchronous way, so that a transfer of two protons occurs, which involves two neighboring water molecules connected by a hydrogen bond and a surface Si atom. In Fig. 7 two snapshots of the water reaction before and after the proton transfer are presented: molecule 1 is physisorbed to one Si atom and makes a hydrogen bond with molecule 2; subsequently, the H atom involved in the H-bond is transferred from molecule 1 to molecule 2, which releases a hydrogen atom in order to remain neutral. H then bonds to a nearby Si atom. It is relevant to note that at variance with the dissociation of a water molecule observed at low coverage, in this case the -OH and -H fragments are not bonded to two neighboring Si atoms. A similar proton transfer mechanism has been observed in the *ab initio* MD study of water molecules on alumina⁶, which, similar to SiC, presents polar surfaces. However, in the case of alumina, a temperature of 300 K was needed in order to observe the transfer, while in the case of Si-SiC, surface proton transfer occurs unexpectedly at extremely low temperatures (the maximum temperature of our simulations is 50 K).

The results discussed above show that full hydroxylation of the surface should be energetically favored: the high density of -OH groups formed at the Si-terminated surface upon water adsorption is expected to enhance the surface hydrophilicity and represents a first step towards surface functionalization. Indeed the Si-OH (silanol group) can form hydrogen bonds and then interact efficiently with water: we have estimated that the strength of H bonds between this group and a water molecule is -0.17 eV/bond (-3.9 Kcal/bond) or -0.27 eV/bond (-6.2 Kcal/bond), when it functions as a proton acceptor or proton donor respectively (note that the hydrogen bond between two water molecules is about -0.20 eV/bond, i.e. -4.7 Kcal/bond)³¹.

D. Calculation of vibrational frequencies.

We have estimated the stretching frequencies of the modes originating from the water dissociated radicals (O-H and Si-H stretching modes), in the frozen phonon approximation, and including

anharmonic terms. Frozen phonon calculations were performed in the same supercells as the other simulations described here, i.e. including only the Γ point of the supercell BZ. By comparing the results obtained for the stretching mode of one single bond as obtained using supercells of different size, we estimate an error of $\sim 45 \text{ cm}^{-1}$ on the mode frequencies, induced by k-point sampling (when using the 16 atoms/layer supercell, four non-interacting replicas of the same bond can be simulated at each surface, thus providing a 4 k-point sampling). Therefore the calculations of vibrational frequencies presented here are intended to give qualitative and not quantitative and exhaustive results.

For each mode, we started from the equilibrium position of the dissociated radical and surface, then we performed several calculations at different bond elongations (8 in the range $\pm 10\%$), in order to obtain a potential energy curve and to estimate the mode frequency with a fourth order degree polynomial³²: in this way, both the harmonic and anharmonic contributions to the frequency can be evaluated, the latter becoming relevant because of the small hydrogen mass. We did not attempt to include zero point energy corrections.

In agreement with similar calculations performed for hydrogen-containing radicals in other semiconductors³², we found that the anharmonic term ($\Delta\omega$) is significant for both the O-H and Si-H stretching modes, and tends to decrease the harmonic value (ω_0). In particular we found that the –OH stretching mode at $\frac{1}{4}$ ML coverage is 3289 cm^{-1} ($\Delta\omega = -162 \text{ cm}^{-1}$), while it becomes 3195 cm^{-1} ($\Delta\omega = -188 \text{ cm}^{-1}$) at 1ML coverage; thus a softening of the mode with larger anharmonic contributions takes place, due to the H-bond interaction. The variation in frequency is consistent with experimental results³³ showing a difference of $\sim 150 \text{ cm}^{-1}$ between isolated and H-bond interacting silanol stretching frequencies. As for the Si-H bond, we estimate a frequency ω_0 of 2134 cm^{-1} ($\Delta\omega = -38 \text{ cm}^{-1}$). Our results are consistent with the IRAS data of Amy F. et al¹³, who obtain a frequency of 3695 and 2105 cm^{-1} for the O-H and Si-H stretching modes respectively when exposing to water the overstoichiometric Si-SiC(001)-3x2 surface. The higher frequency obtained in the experiment for the –OH stretching mode is consistent with the weakening of the –OH bond observed in our case: indeed in Ref. 13 –OH is attached

to a Si atom bonded to a Si underlying atom, while in the present case the underlying layer is composed of C atoms which have higher electronic charge polarization.

IV. Water adsorption at the C-SiC(001) Surface

A complete different reactivity with water molecules has been found when exposing a carbon terminated SiC plane to water. In this case, for every tested adsorption site, we found that the molecule leaves the surface and, at the end of the simulation, remains floating well above the substrate: the final C ... O distances are 3.1-3.3 Å and the C ... H distances are 2.6-2.9 Å; such distances are large enough to leave the surface reconstruction nearly unperturbed. This is confirmed by total energy calculations, which yield a zero energy difference between the converged system, and the unreacted constituents. Thus, similar to the C(001) diamond surface⁴, water molecules do not form a molecular physisorbed state on the C-SiC(001) surface. Such behaviour has also been observed at high coverage (1ML), in which case the water molecules move to optimise the hydrogen bond network, without interacting with the underlying surface atoms. At low coverage, if the water molecule is pushed towards the surface carbon atom at a distance lower than 1.5 Å, thus overcoming a rather large barrier, it quickly dissociates with the -OH and -H fragments bonded to the two different C atoms of the surface dimer, with an energy gain of -1.4 eV/molec (31.6 Kcal/mol). Upon dissociation, the attached C-C dimer is elongated up to 1.36 Å, thus being sp^2 hybridized, and it has a buckling of 2.4° ($\Delta z = 0.03$ Å) with the C atom bonded to the oxygen atom in upper position (C-O 1.40 Å). Correspondingly, the Si-C bonds between the dimer and the subsurface layer are also changed and become 1.93 and 1.87 Å long. The other C-C surface dimers are unchanged while the Si-Si subsurface dimers close to the attached molecule are only slightly elongated (2.47 Å). In order to estimate the energy barrier for this reaction, we performed a 10 step constrained molecular dynamics starting with a water molecule facing C-dimers, with an -OH bond parallel to the surface, and increasing O-H distance (d_{OH}). At each step, all the atoms were allowed to relax, while keeping d_{OH} constant. The energy barrier along this path is larger than 1.0 eV/molec (23.1 Kcal/mol), which reveals that even at high temperature the reaction does not proceed spontaneously and the water molecules do not react with this surface. This behaviour closely resembles the reactivity of the

(001) surface of diamond, for which it was found that water molecules do not form a molecular precursor; moreover dissociation can occur being and is an extremely exothermic (-2.7 eV/molec, -63.0 Kcal/mol) and activated process (high activation barrier of 1.1 eV/molec - 25.8 Kcal/mol), as shown both theoretically and experimentally⁴. Nevertheless, while the diamond surface is left with single C-C bond upon water dissociation, the C-SiC(001) one still presents strongly bonded sp^2 carbon atoms, which give rise to a so called ‘enol’ structure, where an –OH group is bonded to an unsaturated C-C bond. These results show that at variance with the Si-SiC surface, the carbon terminated substrate is highly inert towards a wet ambient and is hydrophobic, due to the high stability of the triple bonded C-C surface dimers.

V. Further oxidation of SiC surfaces

Finally we analyzed further possible oxidation steps of the surface in wet ambient for both the Si- and C- terminations, using total energy minimization. In this case, we did not attempt to find transition states or to evaluate the reaction path for further dissociation of the –OH group. In particular, for the Si terminated surface, we considered the insertion of the oxygen atom of the -OH fragment in the Si-Si dimer bond with the formation of a bridged oxide (Si-O-Si) as shown in Fig. 8. In the final product two Si-H bonds (1.50 Å) and two Si-O bonds (1.67 Å) are formed. The Si atoms involved in the reaction nearly recover their bulk position in a tetrahedral coordination, while the oxygen atoms becomes sp^2 hybridized (Si-O-Si = 121.8°). The energy gain upon insertion of the oxygen atom in the surface silicon dimer is -1.03 eV/molec; in a similar fashion, this reaction is favorable at the Si(001) surface ($\Delta E = -1.3$ eV/molec at B3LYP level³⁴). Our findings are in good agreement with recently published results¹³, where experimental evidences of O-Si-O structure formation were found.

For the C-SiC(001) surface we have considered the isomerization of the starting dissociation product to a carbonyl or ether group (see Fig. 9). The carbonyl configuration, where the double bond of the C dimer is broken to favor formation of a double C-O bond, is almost degenerate with the starting geometry; in the relaxed structure a C-O bond 1.23 Å long is found, while the C surface dimer is elongated up to 1.55 Å (buckling $\Delta z = 0.03$ Å). Furthermore the SiC bonds connecting the carbon dimer

to the subsurface Si layer are elongated up to 1.9-2.0 Å. The ether group formation, with the oxygen bridging two carbon atoms (O-C 1.35 Å and C-H 1.09 Å), is highly unfavorable ($\Delta E = 2.08$ eV/molec - 48.0 Kcal/mol). These two oxidation products are both favored at the diamond (001) surface, with a reaction energy of -0.42 eV/molec and -0.45 eV/molec for the carbonyl and ether group respectively (according to cluster calculations performed with various exchange and correlation functionals⁴). Our findings are in agreement with the experimental observation that only the Si terminated surface of β -SiC gives rise to a stable oxidized surface³⁵.

VI. Conclusions

We have presented a detailed study of the interaction of water molecules on SiC(001) surfaces. Our findings reveal that water dissociates on the Si-terminated surface, at all coverages, enhancing the surface hydrophilic character, while the C-terminated surface is hydrophobic. This suggests that by growing SiC substrates with adjacent islands which are either Si- or C-terminated an atomic control of hydrophilic and hydrophobic environments may be attained. This could be realized by epitaxial growth of cubic SiC substrates which are preferentially Si-terminated and by subsequent deposition of, e.g. C_2H_4 groups on masked islands, along the lines proposed by J. P. Long et al.³⁶. Controlling wetting properties of a surface by patterning regions with hydrophilic and hydrophobic characters is very important for the attachment of DNA and proteins and the realization of sensors^{1,37-38}. For example, pure DNA strand attachment is very efficient on surfaces which show a hydrophobic/hydrophilic patterning, since the hydrophobic interaction with aqueous DNA solutions prevents DNA attachment between the elements of an array and thus acts as a barrier for diffusion of DNA between array elements^{1,38}. In addition, in conventional bio-array applications using Si or SiO_2 surfaces, biomolecules are first adsorbed on specific regions and the remaining surface areas are covered with hydrophobic molecules to prevent non-specific bindings during the subsequent assays. This so called blocking step may affect the adsorbed biomolecules, and in particular introduce random fluctuations in their density. A non-controllable density would produce a random reading of the array and would prevent any quantitative analysis. It is therefore important to control hydrophobic/hydrophilic patterning at the nanoscale, for a

successful fabrication of high-density arrays of nanometric size. The use of SiC patterned surfaces could facilitate such a control, *prior* to biomolecules adsorption. Finally the use of SiC-based biosensors would open the way to applications where the requirement of biocompatibility is more crucial than for DNA arrays, i.e selective bio-organism capture³⁹ and drug testing.

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FIGURE CAPTIONS

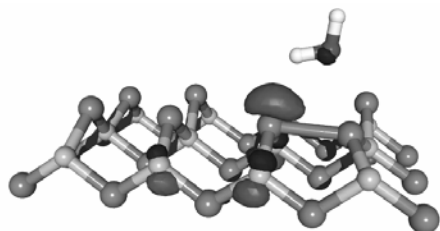


Figure. 1. A snapshot of *ab initio* MD simulation runs at $\frac{1}{4}$ monolayer water coverage on the silicon terminated SiC(001) surface (side view). Charge polarization at the Si-dimer is shown. Only the uppermost substrate layers are shown for clarity; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

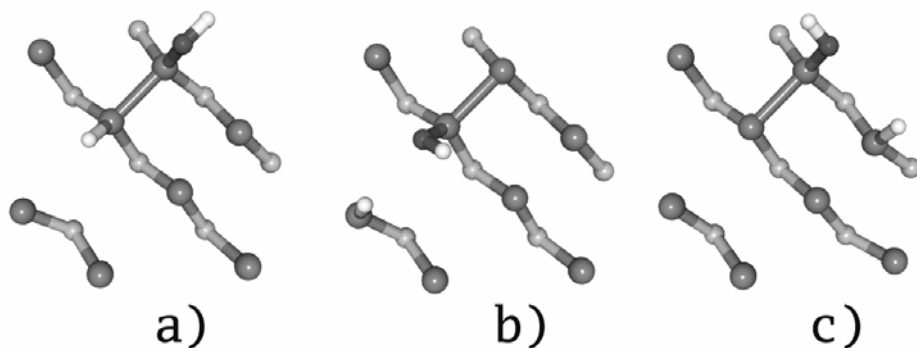


Figure. 2. The three metastable configurations obtained at $\frac{1}{4}$ monolayer water coverage on the silicon terminated SiC(001) surface, represented in top view, and in increasing energy ordering from left to right: a) is the most stable configuration in Si(001), while c) is the most stable at Si-SiC. Only the uppermost substrate layers are shown for clarity; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

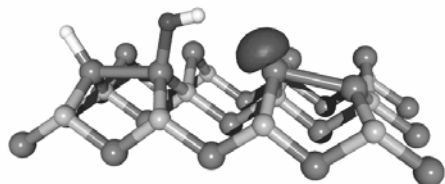


Figure. 3. Dissociation product at $\frac{1}{4}$ monolayer water coverage on the silicon terminated SiC(001) surface (side view, case a) of Fig. 2): charge polarization at the Si-dimer responsible of the H-like bond formation through -OH and the adjacent Si-dimer is shown. Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

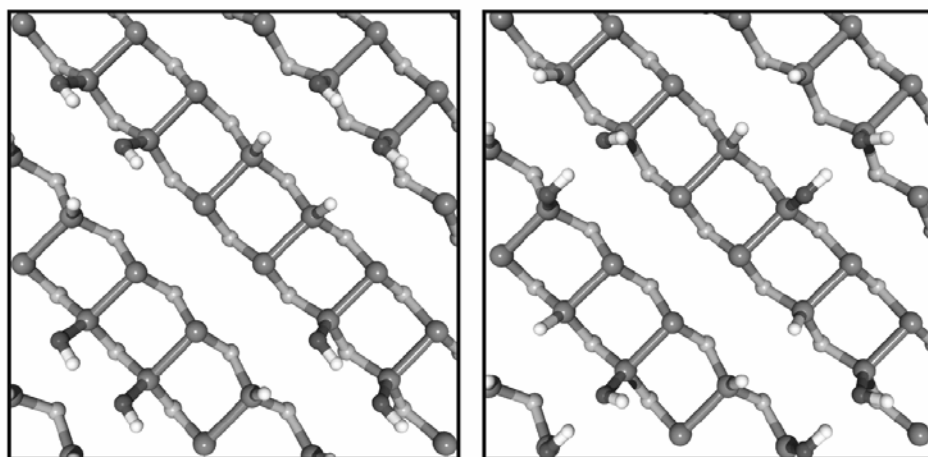


Figure. 4. Top view of two configurations at $\frac{1}{2}$ monolayer water coverage on the silicon terminated SiC(001) surface: on the left hand side, H-bond formation occurs along the substrate dimer rows, while on the right hand side it occurs in the trenches, giving rise to a more favorable structure. Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

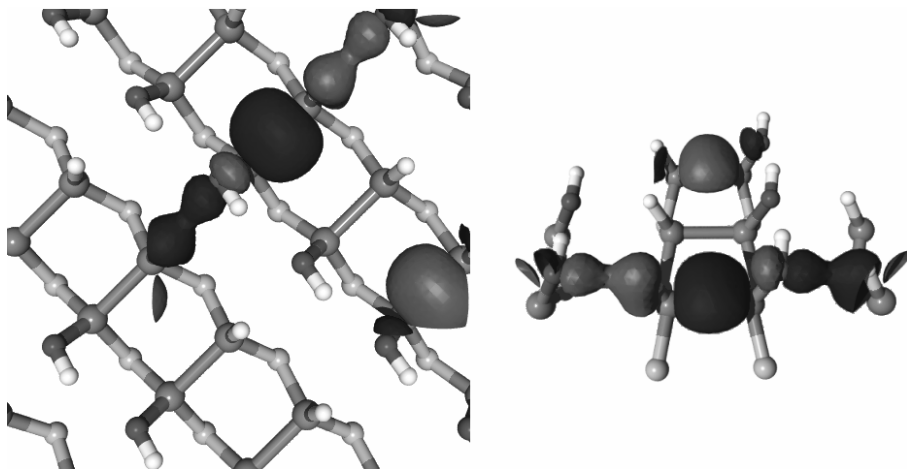


Figure. 5. Isosurface of one of the highest occupied states at full water coverage on the silicon terminated SiC(001) surface, top (left hand side) and side (right hand side) view. Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

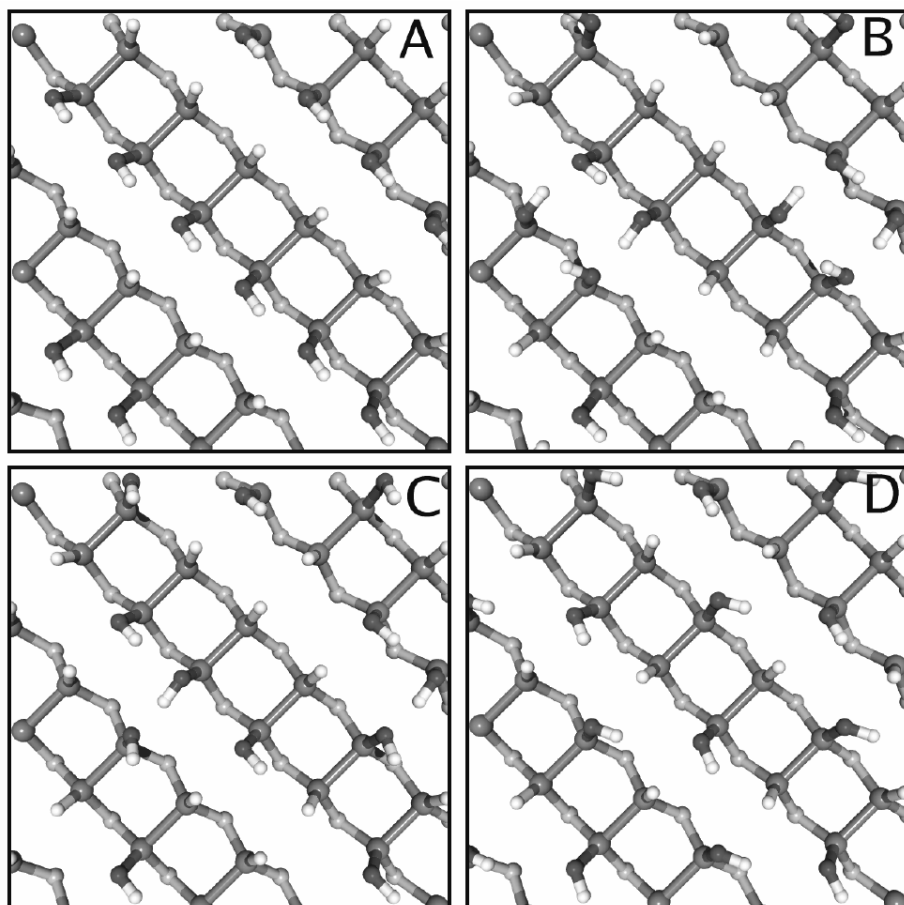


Figure. 6. Top view of the four configurations at full water coverage (see text) on the silicon terminated SiC(001) surface: the top-left panel shows the ordered dissociated structure (H-bond formation occurs along the substrate dimer rows); the top-right panel represents an almost degenerate structure with a maximized number of H-bonds. The two bottom panels show the other configurations in decreasing energy ordering. Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

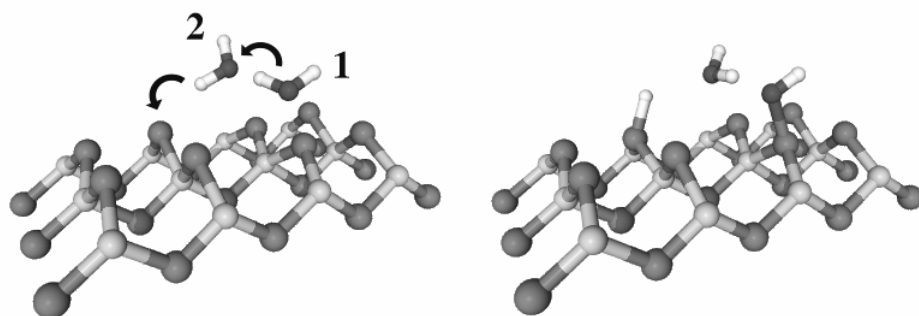


Figure. 7. Proton transfer reaction mechanism (H-bond mediated) for water dissociation at full coverage on the silicon terminated SiC(001) surface: two successive snapshots of the dissociation are shown. Only the two molecules involved in proton exchange during this time interval are represented: on the left, molecule 1 is physisorbed to one Si atom and forms a hydrogen bond with the other molecule; the proton involved in the H-bond is exchanged between the two molecules, and molecule 2 releases a hydrogen atom in order to remain neutral. This H atom is eventually bonded to a nearby Si atom. Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

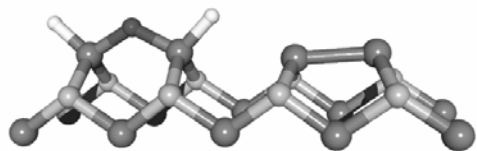


Figure. 8. A possible scheme of wet oxidation of the silicon terminated SiC(001) surface (side view). Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

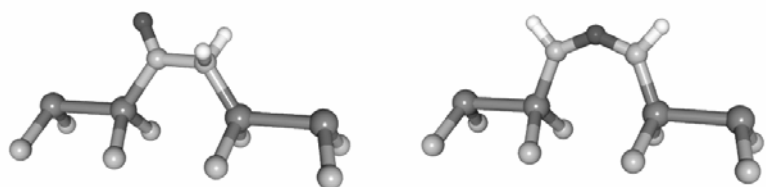


Figure. 9. Carbonyl (left) and ether (right) formation at the carbon terminated SiC(001) surface. Only the uppermost substrate layers are shown; dark (light) grey spheres in the substrate represent silicon (carbon) atoms, while dark (light) grey spheres in the adsorbate represent oxygen (hydrogen) atoms.

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